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Seawater's organic polymers – how to behave on mercury drop?

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Carbohydrates, proteins and lipids are the main groups of organic compounds found in seawater. They represent 20% of organic matter present in natural waters and are compounds of small molecular mass characterized on molecular level in plankton and sediments. Phytoplankton is the highest producer of organic matter in seawater's photic zone. Polymeric organic material, mainly composed from polysaccharides (PS), represents the main fraction (up to 80%) of phytoplankton exudates.

Catalyzation proceses of:

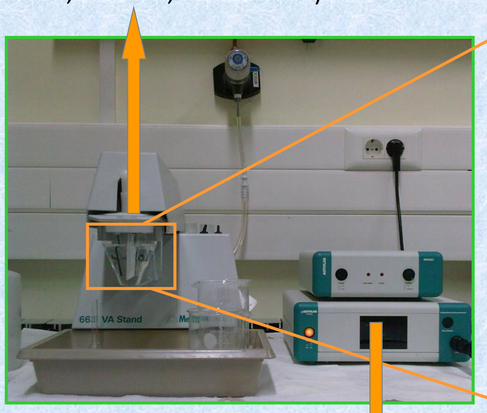
- **protein human serum albumin (HSA),**
- **polysaccharide ι-carageenan and**
- **polymers in seawater samples**

were analyzed by constant current chronopotentiometric stripping analysis (CPSA) method.

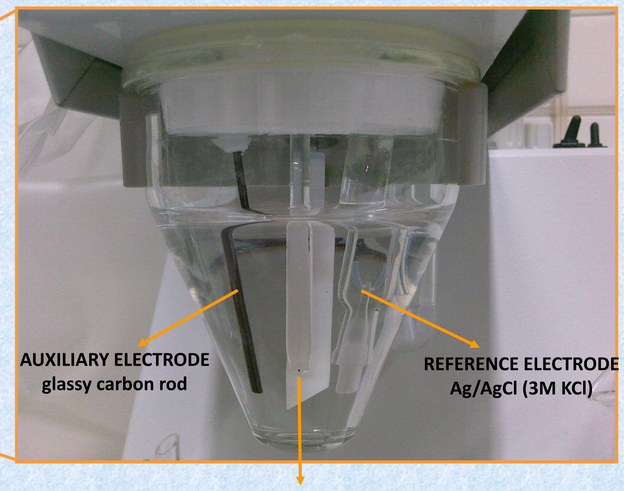
Why peak "H" ?
Catalytic ***h***ydrogen evolution
High sensitivity
Heyrovsky

ELECTROCHEMICAL INSTRUMENTATION

663 VA Stand multimode system
(Metrohm, Herisau, Switzerland)



μ-Autolab Analyzer
(EcoChemie, Utrecht, The Netherlands)

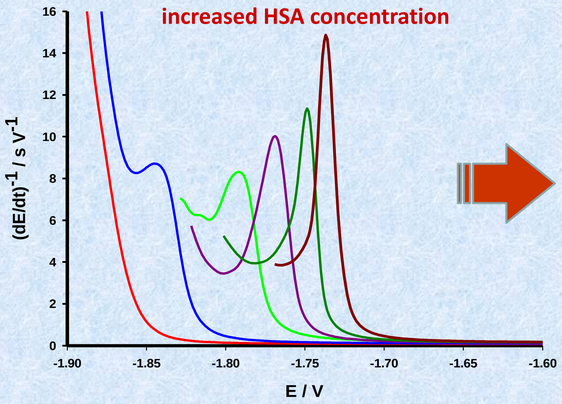


ORGANIC CATALYST OF HYDROGEN EVOLUTION ON MERCURY DROP

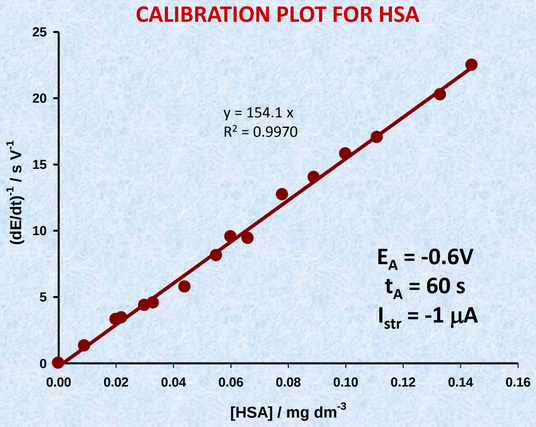
N-POLYMERIC ORGANIC MATERIAL (N-POM)

electrolyte: "organic matter free" seawater

"PEAK H" of increased HSA concentration

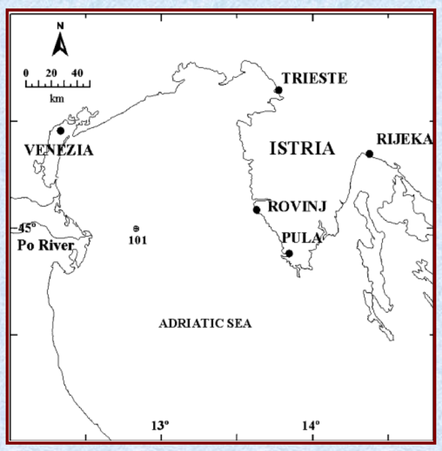


CALIBRATION PLOT FOR HSA



Concentrations of N-POM, surface active substances (SAS) and dissolved organic carbon (DOC) measured in seawater samples from Northern Adriatic station 101.

date of sampling	depth / m	N-POM -E_p / V	N-POM $(dE/dt)^{-1}$ / s V^{-1}	N-POM eq. μg HSA dm^{-3}	SAS eq. mg T-X-100 dm^{-3}	N-POM / SAS	DOC mg C dm^{-3}	N-POM / DOC
6 June 2008	0.5	1.746	9.3	60	0.192	0.31	1.57	0.038
	~31	-	0	0	0.088	0	1.04	0
26 June 2008	0.5	1.736	11	71	0.363	0.19	1.85	0.038
	~31	-	0	0	0.136	0	1.35	0
20 October 2008	0.5	1.791	2.8	18	0.251	0.072	1.01	0.018
	~31	1.780	0.30	0.2	0.214	0.00091	0.80	0.00025
17 January 2009	0.5	-	0	0	0.102	0	1.01	0
	~31	-	0	0	0.055	0	1.09	0
17 March 2009	0.5	1.772	4.7	30	0.165	0.182	1.25	0.024
	~31	1.805	1.5	9.6	0.073	0.13	0.94	0.010



Sampling station 101 in Northern Adriatic Sea

N-POM IN SEAWATER SAMPLES

part of SAS and DOC
variable through the seasons:
higher for season of increased biological production (June 2008)
lower for winter samples (January 2009)

CPSA

sensitive method for measurement of presodium "peak H "
qualitative and quantitative determination of N-POM in seawater

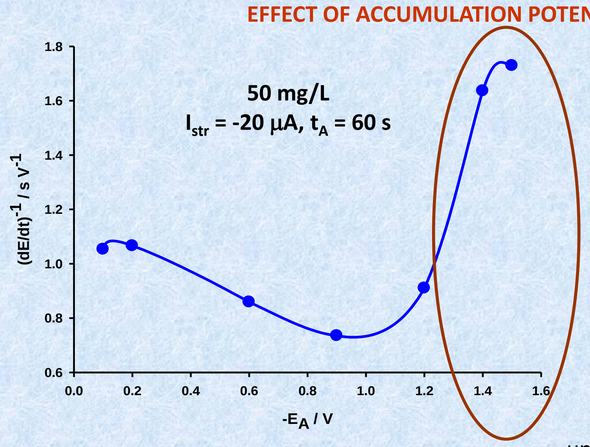
Peak H

additional parameter for the characterization of natural organic matter
measured without any sample pretreatment

SULPHATED POLYSACCHARIDES

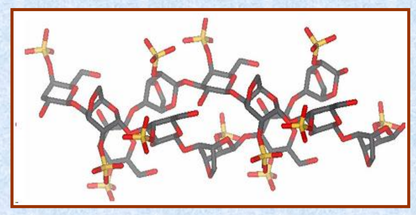
electrolyte: 0.55 M NaCl + 0.5 M acetate buffer

EFFECT OF ACCUMULATION POTENTIAL ON ι-CARRAGEENAN'S "PEAK H_{PS}"



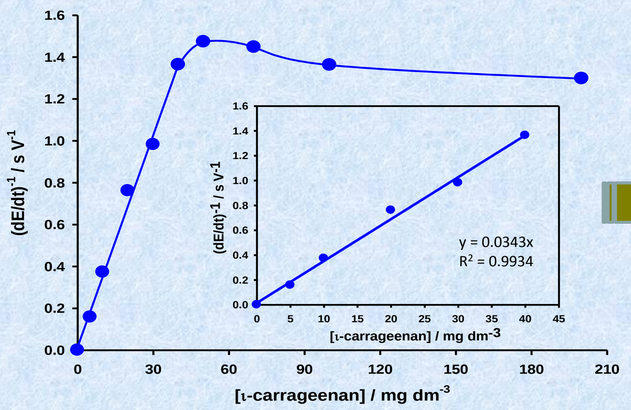
ι-CARRAGEENAN 3D STRUCTURE

threefold, righthanded, half-staggered, parallel double helix stabilized by interchain hydrogen bonds



E_A < -1.4 V
uncoiling of double helix – releasing of catalytically active groups previously hidden in the structure

CALIBRATION PLOT FOR ι-CARRAGEENAN



E_A = -0.1V
t_A = 60 s
I_{str} = -20 μA

DETECTION LIMIT FOR ι-CARRAGEENAN
4.1 mg dm^{-3} i.e. 8.2 nM

POLYSACCHARIDES WITH SULPHATED GROUPS

electrochemically active molecules
produce at mercury drop electrode in buffered electrolyte
"PEAK H_{PS}" which is due to the catalytic hydrogen evolution

SULPHATE RESIDUE

new type of groups responsible for the electrocatalysis

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